

Appendix A
Laboratory Prescreening for Chemical Selection

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4.1 Objectives

Previous testing work has established the suitability of alum and ferric iron salts for precipitation/adsorption of phosphorus to the low ppb range. Previous testing has also established the appropriate pH ranges for carrying out these reactions and minimizing the quantity of residual soluble metal in the treated water. The intent of this prescreening testing was to verify earlier testing results and to determine the starting point conditions for pilot testing. The objectives of the prescreening testing were as follows:

- Verify coagulant dosage/pH relationship versus residual P and residual soluble metal.
- Select the appropriate flocculation polymer(s) and starting dosage(s) for use at the pilot scale.
- Simulate solids contact in the laboratory and observe solids settling characteristics and supernatant quality.
- Simulate sludge storage in the laboratory and observe whether objectionable feedback of P or residual metal occurs over time.

4.2 Technical Approach

Both alum and ferric chloride were evaluated on two source waters: STA influent (NEAA), and STA effluent (SSTA). Ferric chloride was selected as the iron coagulant to be tested because: 1) previous testing efforts on colored humic acid surface waters have not shown a measurable difference between ferric sulfate and ferric chloride treatments, and 2) effects of sulfate ion in the treated water were already being evaluated with the alum treatment — using ferric chloride allows evaluation of effects from chloride residuals in the treated water stream.

All testing except the sludge storage evaluation was conducted using a standard jar testing apparatus and 2-liter square beakers at the District's Skees Road Laboratory facility. Sludge storage testing was conducted at the South ENR Supplemental Test Site. This section describes the general technical approach used for conducting various tests. Specific standard procedures

for feedstock collection, batch jar testing, and solids contact jar testing procedures are described in Section 4.3.

The testing was conducted in a sequential manner to 1) verify optimum coagulant dose and its effect on pH and residual metals concentrations 2) Select appropriate polymer products and optimize dosage for startup at the pilot scale, 3) simulate the solids contact reaction and observe solids characteristics at the higher solids concentrations and repeated polymer dosing that are expected in the pilot-scale, and 4) simulate solids storage and observe whether objectionable feedback of P or residual metal occurs over time.

The technical approach and testing sequence were as follows:

1. **Lab Orientation and Safety Meeting.** MWTS Contract staff received a lab tour and safety orientation covering the District's safety policies and procedures. The training took place Monday, March 8, 1999, at the Skees Road laboratory. Following the orientation, staff set up testing apparatus, calibrated equipment, and inventoried chemicals. Staff collected the first samples from the ENR wetlands sites, and transported test aliquots to the laboratory.
2. **Coagulant Dose Optimization (Metal and P residual) and Effect on pH.** Raw influent waters were titrated using standardized acid and the coagulants to determine acid/base requirements for each jar. A single anionic flocculant was selected to enhance solids settling, and was used for all jar tests at the 0.5 milligrams per liter (mg/L) dosage level. There were six coagulant doses for each water source and each coagulant. Coagulant dosage was 0.25, 0.5, 0.75, 1.0, 1.5, and 2.0 milli-equivalents per liter (meq/L) (lowest dosage was determined as the lowest dosage at which flocculation was observed in the prescreening test). The tests were performed within the optimum pH range for each coagulant at near neutral conditions (6.5 to 7.0 SU [standard units] for alum, 7.0 to 8.0 SU for iron). Following flocculation, samples were collected at the 10 cm depth after 5 minutes for turbidity measurement. The jars were again sampled at time 20 minutes, filtered through 0.45 micron filters, and analyzed for total dissolved P, dissolved metal, dissolved color, and dissolved TOC. This matrix resulted in approximately 28 jar tests.

$$\begin{aligned}(2 \text{ sources}) \times (2 \text{ coagulants}) \times (6 \text{ coagulant doses}) \times (1 \text{ polymer dose}) &= 24 \text{ jars} \\ &+ 10 \% \text{ replication} = \underline{4 \text{ jars}} \\ \text{Total} &= 28 \text{ jars}\end{aligned}$$

Samples for dissolved P analysis were approximately:

$$28 \text{ experiment} + 3 \text{ duplicate} + 3 \text{ spike} + 3 \text{ blanks} = 37$$

3. **Polymer Screening for Selection of Polymer Product(s).** This testing consisted of comparing the effects of various polymers on turbidity reduction at varying surface loading rates. The intent was to select a polymer product for each of the coagulants that effectively flocculated colloidal material and pin floc. Three products were tested. The products were tested until an effective product was found for each coagulant and source water combination. The coagulant optimization results were not available, therefore the coagulant dose was set at 1 meq/L for the screening step. Polymer doses were 0.0, 0.25 and 0.5 mg/L. Samples were collected at times 1, 2, 5 and 10 minutes after the flocculation period ended at a depth of 10 cm below the initial liquid surface. The samples were measured for turbidity. This matrix resulted in approximately 24 jar tests:

$$(2 \text{ sources}) \times (2 \text{ coagulants}) \times (1 \text{ coagulant dose}) \times (2 \text{ polymers}) \times (3 \text{ polymer doses}) = 24 \text{ jars}$$

Samples for turbidity analysis were approximately:

$$(24 \text{ jars}) \times (4 \text{ SLR times}) + 2 \text{ raw} + 10 \text{ duplicate} = 108$$

4. **Polymer Dosage Optimization.** Polymer dosage was optimized using the selected polymer from step 3 at the optimum coagulant dose(s) for each source water and for each coagulant. The polymer dose was varied between 0 and 0.7 mg/L. Samples for turbidity analysis were collected at times 1, 2, 5 and 10 minutes after the flocculation period had ended at a depth of 10 cm below the initial liquid surface. The two best settling jars from each coagulant/source water test had additional sample volume drawn at 10 minutes settling time and were analyzed for TP, dissolved TP, dissolved Ortho-P, dissolved metal, dissolved color, and dissolved organic carbon. This matrix resulted in approximately 24 jar tests:

$$(2 \text{ sources}) \times (2 \text{ coagulants}) \times (1 \text{ polymer}) \times (6 \text{ polymer doses}) = 24 \text{ jars}$$

Samples for turbidity analysis were approximately:

$$(24 \text{ jars}) \times (4 \text{ SLR times}) + 2 \text{ raw} + 10 \text{ duplicate} = 108$$

Samples drawn for total P analysis were approximately:

$$(2 \text{ samples/exp} \times 4 \text{ experiment}) + 2 \text{ raw} + 1 \text{ duplicate} + 1 \text{ spike} + 1 \text{ blank} = 13$$

5. **Solids Contact Simulation.** The solids contact reaction was simulated for each coagulant on each feed water in order to evaluate the behavior of the floc and the quality of the overlying supernatant as solids are recycled in the system and polymer dosage/charge begins to

concentrate. This testing consisted of using the optimum dose of coagulant and polymer in a sequential set of jar tests. The preceding jar was allowed to settle and the solids removed and added to the beginning of the flocculation period of the next jar in the sequence. A detailed procedure for solids contact simulation is provided in Section 4.3.3.

Solids Storage Evaluation. A sufficient quantity of sludge solids was generated to conduct a solids storage evaluation. The intent of this evaluation was to discern whether the solids generated are prone to digestion and flotation over time, and whether there is the potential for significant feedback of P or metal from the solid to the liquid phase. The low-P feed (SSTA) water was used with two coagulants. Approximately 2 to 3 gallons of settled sludge for each test (alum and iron) was produced using continuous flow pilot equipment procured for the CT/SS study at the supplemental technologies sites. Sludge was produced using the optimized coagulant and polymer dosages determined from the Skees Road Lab jar testing. The solids were stored with approximately 7 to 8 gallons of overlying treated water in 10-gallon rectangular aquariums in the PSTA/MWTS trailer. The reactors were kept at room temperature, away from direct sunlight. Reactor volume lost to sampling and to evaporation was replaced using distilled water. The sludge from each reactor was sampled monthly and analyzed for TP and TSS. The water column was sampled concurrently and analyzed for TP, TDP, and dissolved metal (Al or Fe), and monitored for pH, turbidity, temperature, and dissolved oxygen. The supernatant was sampled every 2 weeks and analyzed for dissolved total P. After the reactors were sampled (every 2 weeks), the contents were thoroughly mixed by hand and allowed to resettle.

4.3 Standard Testing Procedures

4.3.1 Feedstock Collection

Samples representative of EAA effluent (NEAA) and STA effluent (SSTA) were collected from the feed reservoirs at the North and South ENR test sites. Approximately 35 gallons were required from each site. To ensure fresh samples, aliquots were collected on Monday for tests conducted Tuesday and Wednesday; fresh aliquots were collected on Wednesday for use in the tests conducted Thursday and Friday. Approximately 25 gallons were collected from each site at each sampling event. Samples were collected using a centrifugal pump, with the suction line submerged approximately 2 ft below the surface of the reservoir at the vicinity of the bar screen. Samples were collected in 5-gallon polyethylene carboys. The carboys were rinsed 3 times with the sample solution prior to sample collection. The samples drawn from the north ENR site were referred to as NEAA. The samples drawn from the South ENR site were referred to as SSTA. Samples not needed immediately were stored in the walk in cooler at the Skees Rd. Lab. Samples used within approximately 24-hours were stored at room temperature in the lab.

An initial influent composite of each of the NEAA and SSTA waters was analyzed for pH, TP, TDP, dissolved orthophosphate, alkalinity, dissolved organic carbon (DOC), turbidity, color, dissolved iron and aluminum, and total suspended solids (TSS).

4.3.2 General Jar Testing Procedure

Testing was carried out using procedures described by Hudson and Wagner (1981) for conventional jar testing. The procedure described in Section 4.3.3 was used to conduct solids contact testing in the jar test apparatus. Prior to jar testing, the raw water samples were titrated with the coagulants and acid to determine alkalinity and the acid/base requirements for each specific jar. Commercial grade reagents (coagulants, acid/base, polymers) were used throughout the testing.

4.3.2.1 Filling

Two-liter square beakers were used with a standard six-place Phipps and Bird gang stirrer. The feedstock carboy was mixed and the test beaker(s) filled to the 1-liter mark. The feedstock carboy was then remixed and the volume of the beakers was raised to the full 2-liter mark.

4.3.2.2 Dosing

Rapid mixing was conducted at 200 revolutions per minute (rpm) ($G > 200\text{s}^{-1}$ in square 2-liter beakers). At 0 seconds the primary coagulant was added at the tip of the mixer blades with a volumetric pipette or syringe. Immediately thereafter the predetermined amount of acid or base was added to achieve the desired pH setpoint by using a volumetric pipette or syringe to deliver the appropriate volume at the tip of the mixer blades. Next the anionic flocculant was added and rapid mixing continued for 15 seconds.

4.3.2.3 Flocculating

Fifteen seconds after the polymer was added the mixing speed was reduced to 34 rpm ($G = 23\text{s}^{-1}$ in square 2-liter beakers). This provided an appropriate energy to form and uniformly suspend particles throughout the flocculation period. The sample was allowed to flocculate for 20 minutes. The pH was trimmed during the flocculation period when necessary. After 20 minutes' flocculation time the mixer was turned off and the mixing blades were removed from the liquid.

4.3.2.4 Settling and Sampling

Samples of treated water for analysis were drawn from the sampling port located 10 cm below the initial liquid surface. Filtered or dissolved sample fractions were prepared by using a peristaltic pump and 0.45-micrometer (micron, or μm) membrane filters.

4.3.3 Solids Contact Simulations

A solids contact simulation was performed with the alum and ferric chloride coagulant dosage and the optimized polymer and dosage determined from the previous testing. This set of tests allowed a qualitative assessment of the solids characteristics, as well as an opportunity to verify residual P and metal concentrations after treatment.

Solids contact was simulated by running sequential jar tests while retaining the sludge produced from previous tests. The estimated hydraulic retention time of liquid in the pilot reactors was expected to be approximately 2 hours. Assuming a minimum target solids retention time of 1 day, the number of batches needed to fully simulate pilot operating conditions was calculated as the solids retention time/hydraulic resident time (SRT/HRT) = $24/2 = 12$ batches.

The procedure utilized two beakers for each of the four source water/coagulant combinations tested. While one beaker was in a rapid mix (reaction) and flocculation cycle, the other beaker was in a settling and decant cycle, so that the solids from the settled beaker were ready to be added to the next reaction beaker. The bottom 400 mL of sample from each previous jar test was returned to the subsequent jar test during the flocculation period.

Rapid mix for the addition of chemicals followed the procedure previously outlined in the standard jar test procedure. Raw influent (1.6 liters) was reacted through rapid mix using the optimum coagulant dose, pH, and polymer doses determined previously. The bottom 400 mL of liquor from the previous jar test was then be carefully added at the start of the flocculation period. Flocculation proceeded for 20 minutes, and settling for a period of 10 minutes.

Solids settleability and supernatant quality were measured after flocculation of the fourth, eighth, and twelfth batches. At each of these intervals, supernatant samples were collected from the sample port at 1, 2, 5, and 10 minutes after settling commenced, and analyzed for turbidity. Both the raw influent sample and the sample collected at 5 minutes after settling for the 12th batch were analyzed for TP, TDP, dissolved ortho-P, residual dissolved metal, DOC, and color. Sludge volume (mL/L) after 30 minutes of settling was recorded, and a measurement of the total sludge production (as TSS) was made.

There were four solids contact tests: 2 source waters * 2 coagulants = 4.

Samples for turbidity/settling velocity analysis were approximately:

$$4 \text{ tests} * 3 \text{ batches each} * 4 \text{ time intervals} + 5 \text{ duplicate} = 53 \text{ samples}$$

Samples drawn for the full set of analytical testing on raw samples and on the final batch were approximately:

2 raw + 4 final + 1 spike + 1 duplicate + 1 blank = 9 samples

4.3.4 Sludge Storage Evaluation

A sufficient quantity of sludge solids was generated using both alum and ferric chloride to conduct a solids storage evaluation. The intent of this evaluation was to discern whether the solids generated are prone to digestion and flotation over time, and whether there is the potential for significant feedback of P or metal from the solid to the liquid phase.

4.3.4.1 Generation of Sludge Solids

The south solids contact system located at the South Supplemental Technologies site at the ENR project site was used to generate sludge solids for the testing. This facility consists of three 200-gallon rapid mix/floc tanks in series followed by a parallel plate separator. The mix/floc tanks are equipped with variable speed mixers to allow user control of mixing intensity. The first tank in the series was used as a rapid mix tank. The following two tanks were used to provide tapered flocculation prior to solids settling. Sludge recirculation was provided from the bottom of the separator to the second mix tank (first floc tank) using a centrifugal pump.

Influent consisted of low-P STA effluent waters. Influent flow rate was generally controlled to between 10 and 12 gpm. Chemicals were fed using diaphragm metering pumps. Chemical doses approximated those optimized in the previous Skees Rd. Lab testing described previously. Coagulants (alum and ferric chloride) were added to a concentration of 1.5 meq/L. Polymer (Cytec A-1849 RS) was dosed at approximately 0.5 mg/L. Caustic was dosed at approximately 40 mg/L as NaOH when using Ferric Chloride as coagulant. Chemicals used were bulk commercial grade, with the exception of caustic. The caustic solution used was made from dried sodium hydroxide/sodium nitrate.

Coagulant was added to the raw influent at a pipeline static mixer immediately prior to entering the rapid mix tank. Coagulant mixing was judged to be excellent. Polymer was made up as a 0.1 percent solution (W/W) and fed into the pipeline between the first (rapid mix) and second (flocculation) mix tanks. The mixing intensity in this area is low, and thus dispersion of the polymer into the coagulated stream was judged to be marginal.

Alum sludge was produced on Wednesday, March 24. Approximately 3,500 gallons of influent were treated in the system, from which approximately 11 gallons of dilute sludge were recovered from the bottom of the solids separator. Iron sludge was produced on Thursday, March 25. Approximately 2,900 gallons of influent were treated in the system, from which approximately 10 gallons of dilute sludge were recovered from the bottom of the solids separator.

4.3.4.2 Sludge Storage Testing

Approximately 4 gallons of thickened alum sludge was transferred to a 10 gallon aquarium and covered with approximately 6 gallons of treated effluent. For the iron test, the 10 gallon aquarium was completely filled with a dilute iron sludge mixture. After 24 hours quiescent settling, the alum storage reactor had a settled sludge volume of approximately 2 gallons, and the iron storage reactor had a settled sludge volume of approximately 3 gallons.

The reactors were stored in the MWTS/PSTA project trailer at the South Supplemental Technologies test site. Reactors were kept at room temperature, away from direct sunlight. Reactor volume lost to evaporation was replaced using distilled water. The sludge from each reactor was sampled monthly and analyzed for TP and TSS. The water column was sampled concurrently and analyzed for TP, TDP, and dissolved metal (Al or Fe), and monitored for pH and temperature. The supernatant was sampled every 2 weeks and analyzed for dissolved total P. After the reactors were sampled (every 2 weeks), the contents were thoroughly mixed by hand and allowed to resettle.

4.4 Analytical Support and Data Management

Analytical methods were as described in the project Quality Assurance Project Plan (QAPP). The District provided 1-day turn around on TP and TDP samples for approximately 30 samples per day for 3 days. This was sufficient to allow appropriate decision-making choices in the first days to complete polymer dosage optimization. Measurement of pH, alkalinity, and turbidity was conducted by the testing staff onsite. All other parameters and all phosphorus determinations in excess of 30 samples per day for 3 days of testing were analyzed by PPB Environmental Laboratories (PPB). PPB provided rapid turn around of sample results for the prescreening testing effort to aid in decision-making. Samples were shipped over-night to PPB via Federal Express in order to receive faxed or verbal results by the evening of the next business day.

Testing conditions, observations, and variables for the tests were recorded in a bound laboratory notebook. Additional information such as chemical MSDS sheets were stored in 3-ring binders. Analytical testing results were distributed to the project manager (Dr. Dunn) and to the lab testing lead (Mr. Mulford) to ensure that these data were adequately archived. Testing results were ultimately summarized in spreadsheet format for presentation in this prescreening technical memorandum.

4.5 Research Schedule

The schedule of activities is shown in Table 4-1 below.

TABLE 4-1
Research Schedule

Description	Activity Date(s)
Mobilization/Lab Coordination	3/1 - 3/5
Laboratory Safety Training	3/8
Sample Collection	3/8

Coagulant Dose Testing	3/9
Polymer Prescreening	3/10
Polymer Optimization	3/11
Solids Contact Testing	3/12
Solids Storage Evaluation	3/24 – 7/22

5.0 Results and Discussion

The following section presents the results of the prescreening testing. This section is divided into subsections titled: Coagulant Dose Optimization (Metal and P residual) and Effect on pH; Polymer Screening for Selection of Polymer Product(s); Polymer Dosage Optimization; Solids Contact Simulation; and Sludge Storage Testing

To equally compare the coagulants used for testing the concentrations in this section are typically expressed as equivalents. Conversions from equivalents to concentrations as metal or compound are presented in Table 1 below for convenience.

Table 1 Equivalent Concentrations of Tested Coagulants

Dose (meq/L)	Al ⁺³ (mg/L)	Al ₂ (SO ₄) ₃ (mg/L)	Alum* (mg/L)	Fe ⁺³ (mg/L)	FeCl ₃ (mg/L)
0.25	2.25	14.25	24.75	4.65	13.50
0.50	4.50	28.50	49.50	9.30	27.10
0.75	6.75	42.75	74.25	13.95	40.60
1.00	9.00	57.00	99.00	18.60	54.10
1.50	13.50	85.50	148.50	27.90	81.20
2.00	18.00	114.00	198.00	37.20	108.20

* - Al₂(SO₄)₃*14H₂O

5.1 Coagulant Dose Optimization (Metal and P residual) and Effect on pH.

This section presents the results of testing designed for selection of a range of coagulant doses to be used initially in the operation of pilot plants for Phase 1 Managed Wetlands Treatment Systems. First the effect of coagulant dose on pH for each of the waters was conducted to determine quantities of acid or base to be added during the jar tests and produce insight to quantities needed for the pilot studies. Second the dose of coagulant was varied to determine the dosage needed to produce good floc formation and settling characteristics, and to evaluate residual P and residual dissolved metal concentrations.

5.1.1 Coagulant Effect on pH

The first testing was conducted to determine the effect of coagulant dose on pH of the source waters. This was accomplished by titration of 0.5 liters of NEAA or SSTA water with 1 N solution of either ferric chloride or alum. The effects of alum and ferric chloride addition on the pH of the NEAA and SSTA waters are shown in Figures 1 and 2, respectively. The two source

waters had similar and relatively high alkalinity at 375 mg/L as CaCO_3 for the NEAA and 402 mg/L as CaCO_3 for the SSTA, and thus produced similar titration curves.

Ferric chloride doses above 0.75 meq/L required the addition of sodium hydroxide to maintain pH in the specified range of 7.0 to 8.0 for testing. During testing it was found that the addition of sodium hydroxide immediately before (as opposed to following) ferric chloride addition produced superior floc characteristics and particle settling.

For alum doses of 0.75 meq/L or less, acid addition was needed to maintain the pH in the specified range of 6.5 to 7.0 SU. Common practice in full-scale operations is to add additional alum to reduce pH to the desired range rather than include sulfuric acid feed systems in facility design. This reduces the capital and operations and maintenance costs associated with an additional chemical feed system. Doses of alum within the range of 0.75 to 1.5 meq/L did not need chemical addition to control pH in the desired range. An alum dose of 2.0 meq/L required sodium hydroxide to maintain the process pH above 6.5. Contrary to the experience with ferric chloride, the addition of sodium hydroxide immediately after alum addition improved process performance.

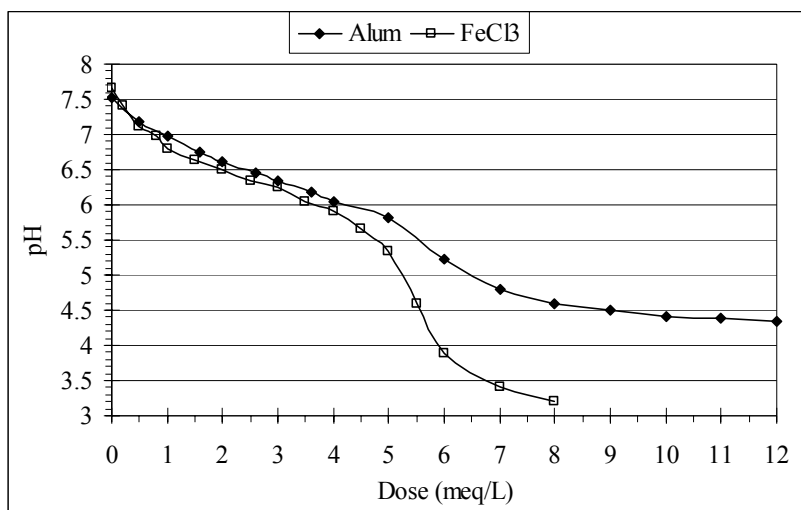


Figure 1 Coagulant Effect On pH Of NEAA Water

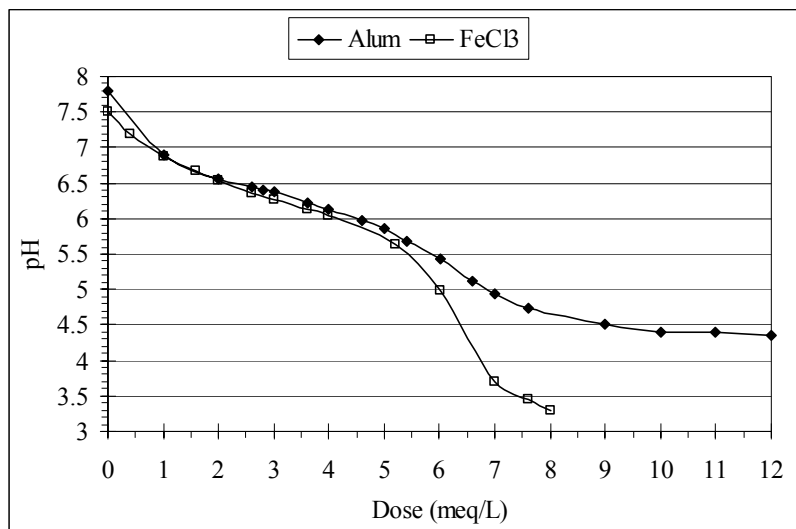


Figure 2 Coagulant Effect On pH Of SSTA Water

5.1.2 Coagulant Dose Optimization

The first set of jar testing was conducted to determine the coagulant dose range that would produce good solids settling characteristics, and to evaluate the residual dissolved P and dissolved metal concentrations at varying coagulant dosages. For each water a series of jars was dosed with alum at 0.25, 0.5, 0.75, 1.0, 1.5 and 2.0 meq/L and an A-1849RS polymer dose of 0.5 mg/L. The series of jar tests was repeated using ferric chloride in place of alum. After a 5 minute settling period samples were collected and measured for turbidity. After a 20 minute settling period samples were collected, filtered at 0.45 μ m and measured for dissolved phosphorus, residual coagulant metal, organic carbon and color.

The process pH for each of the separate jar tests is presented in Figure 3. The pH for each of the waters treated with ferric chloride was maintained between the specified ranges of 7.0 to 8.0 SU, and for alum treatment the specified pH range of 6.5 to 7.0 SU was maintained.

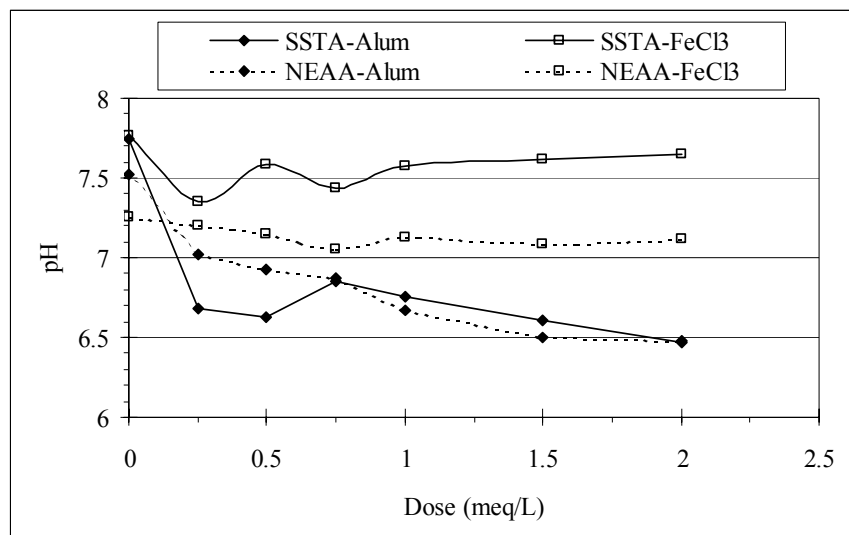


Figure 3 Coagulant Optimization - Process pH

The NEAA and SSTA raw water dissolved total phosphorus (DTP) concentrations were 16 µg/L and 12 µg/L, respectively. The NEAA water DTP was reduced below 10 µg/L with an alum dose of 0.5 meq/L as shown in Figure 4. The DTP was further reduced to a minimum of 6 µg/L with an alum dose of 1.5 meq/L. The NEAA water treated with varying doses of ferric chloride was reduced from the initial DTP concentration of 16 µg/L to 10 µg/L with a treatment dose of 0.25 meq/L. However, the increasing ferric dose produced an increase in the reported DTP concentrations approaching the raw water initial concentration.

The SSTA water DTP was reduced below 10 µg/L with an alum dose of 0.5 meq/L as shown in Figure 4. The DTP was further reduced to a minimum of 5 µg/L with an alum dose of 1.5 meq/L. The DTP concentration of 22 µg/L resulting from treatment with 0.25 meq/L of alum appears to be an outlier caused by contamination. The SSTA water treated with varying doses of ferric chloride increased the reported DTP concentration from the initial average raw water concentration of 11 µg/L to 25 µg/L.

The DTP results indicate that a dose of 0.5 meq/L of alum was sufficient to reduce the phosphorus concentration to below 10 µg/L. The results from ferric chloride were inconclusive in determining the DTP reduction efficiency.

The nature of the increase in DTP using ferric chloride as the coagulant appears to indicate either a treatment chemical had high levels of phosphorus, and/or an analytical interference. The treatments of NEAA and SSTA waters with ferric chloride were repeated using reagent grade sodium hydroxide and similar results of higher than expected total dissolved phosphorus

concentrations in the finished waters were recorded. The comparison of the experimental duplication is presented in the quality control and assurance section of this technical memorandum. It is unlikely that the reagents themselves contributed substantial dissolved P to the treated and filtered effluent. Rather, it appears most likely that some constituent of the ferric chloride coagulant caused a positive interference in the DTP analysis. Sufficient quality assurance sampling was performed to discern that a matrix interference or experimental anomaly is present, though it was beyond the scope of this laboratory prescreening to discern the specific mechanisms. The cause(s) of the apparent interference will be evaluated in greater detail in follow-on testing.

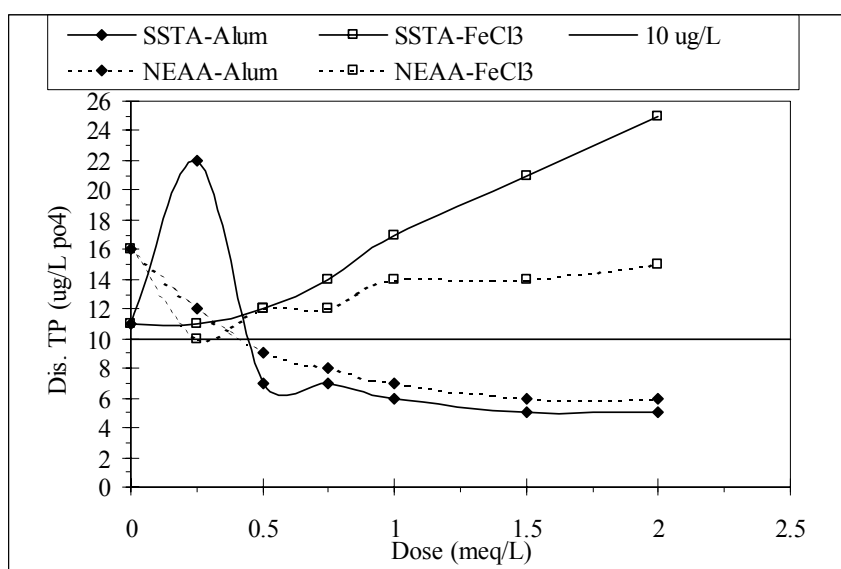


Figure 4 Coagulation Optimization - Dissolved Total Phosphorus

Turbidity was measured at a depth of 10 cm for each coagulant dose after 5 minutes of settling. This measurement corresponds to a particle settling rate of 2 cm/min or a surface-loading rate of 0.5 gpm/ft². Turbidity increased as particle formation increased with dose of coagulant as shown in Figure 5. The raw water turbidity of the NEAA and SSTA water was relatively low at 0.8 ntu and 2.4 ntu, respectively. Particle formation was a characteristic fine pin floc that increased in concentration and size with coagulant dose. Significant particle agglomeration and settling did not occur until a dose of approximately 1 meq/l or greater of coagulant was used. The SSTA water treated with alum that did not produce a significant amount of settleable particles until a dose of 1.5 meq/L was used. Visual observation of the particle formation and settling as well as the quantified turbidity measurements indicated that the process performance was more efficient on the NEAA water than the SSTA water. The results and visual observation indicated that an

anionic polymer dose of 0.5 mg/L and a coagulant dose of 1 to 1.5 meq/L produced acceptable floc formation and particle settling.

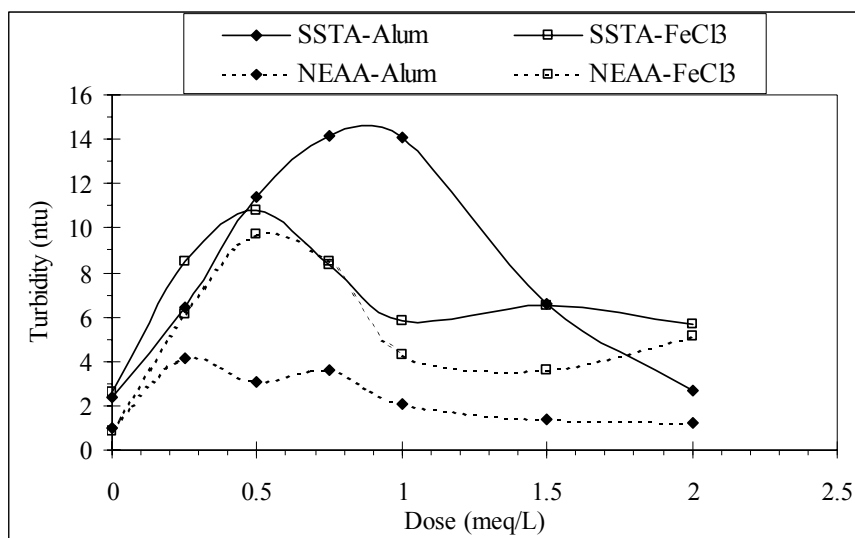


Figure 5 Coagulation Optimization - Turbidity

Dissolved residual iron or aluminum was measured for each jar test of the coagulant optimization and the results are presented in Figure 6. The background aluminum concentrations in the raw NEAA and SSTA waters were similar at 363 and 375 $\mu\text{g/L}$ Al, respectively. The concentration of iron in the NEAA and SSTA waters were 25 $\mu\text{g/L}$ and 10 $\mu\text{g/L}$ Fe, respectively. In general, the residual metal concentration increased with the initial dose of 0.25 $\mu\text{g/L}$ of coagulant and then decreased with the incremental increase of coagulant dose. The residual aluminum and iron concentrations were reduced below background levels for the NEAA water with a dose of 1 meq/L to concentrations of 360 $\mu\text{g/L}$ and 13 $\mu\text{g/L}$, respectively. The SSTA water exhibited a higher residual metal concentration with coagulant dose than the NEAA water. The alum dose of 2 meq/L achieved the background level at a concentration of 374 $\mu\text{g/L}$ Al. The ferric chloride dose of 2 meq/L resulted in a concentration of 13 $\mu\text{g/L}$ Fe or slightly above background.

The results overall indicate that background levels of iron and aluminum for the NEAA water and near background for the SSTA water were achieved at coagulant doses of 1 to 1.5 meq/L. At lower coagulant doses, the level of dissolved metal in the treated effluent begins to exceed the native background concentrations.

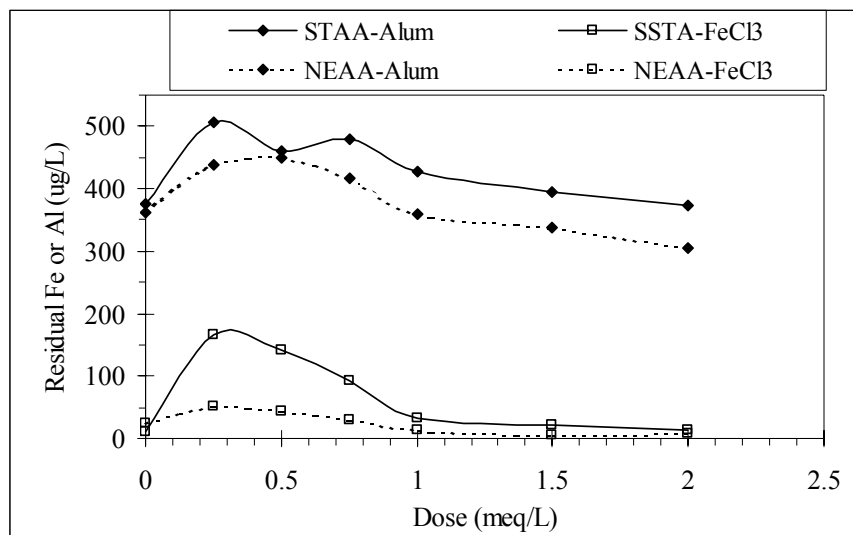


Figure 6 Coagulation Optimization - Residual Metal

Dissolved color was measured for each jar test of the coagulant optimization and the results are presented in Figure 7. The background dissolved colors in the raw NEAA and SSTA waters were 151 and 189 cpu, respectively. The trend in dissolved color reduction with increased coagulant dose was similar for each source water and coagulant. A coagulant dose of 1 meq/L reduced the color by approximately 50 percent. However, the color reduction per coagulant dose was greater with alum than ferric chloride.

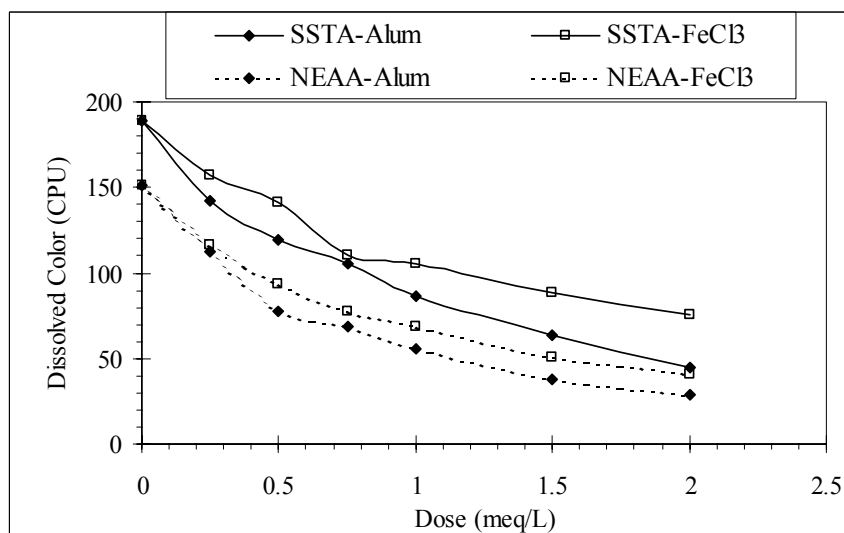


Figure 7 Coagulation Optimization - Dissolved Color

Dissolved organic carbon (DOC) was measured for each jar test of the coagulant optimization and the results are presented in Figure 8. The background DOC in the raw NEAA and SSTA

waters averaged 24 and 32 mg/LC, respectively. In general, the coagulants performed similarly on each water and reduction in DOC did not occur until a coagulant dose of 0.75 meq/L or greater was used. At 2 meq/L coagulant dose, total reduction in DOC was between 25 and 42 percent indicating that the concentration and nature of organic matter required a high dose of coagulant to achieve settleable particle formation. This is consistent with previous researcher's observations when treating waters with significant concentrations of humic acid and significant color bodies.

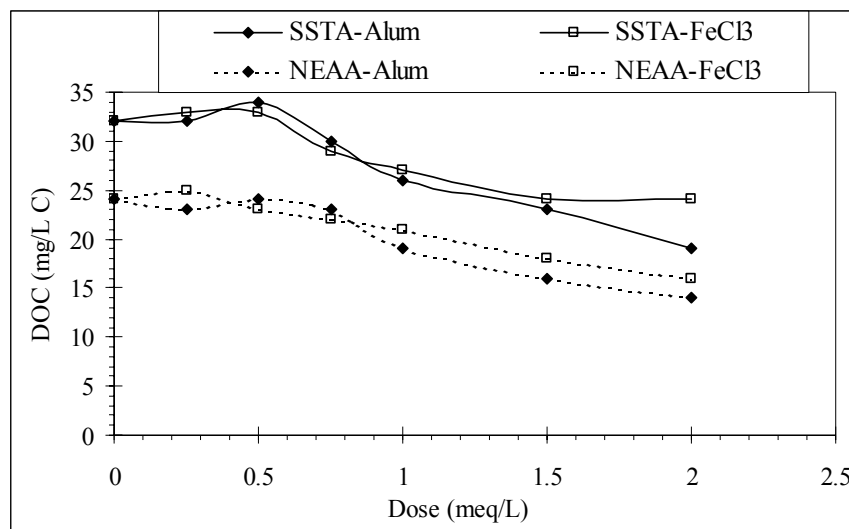


Figure 8 Coagulation Optimization - Dissolved Organic Carbon

The coagulation optimization testing results indicated that a dose of 0.5 meq/L of alum was sufficient to reduce the DTP concentration to below 10 $\mu\text{g/L}$. The results from ferric chloride were inconclusive in determining the DTP reduction efficiency. The turbidity measurements taken after 5 minutes of settling and visual observations indicated that the anionic polymer dose of 0.5 mg/L and a coagulant dose of 1 to 1.5 meq/L produced acceptable floc formation and particle settling. The background levels of iron and aluminum for the NEAA water and near background for the SSTA water were achieved at coagulant doses of 1 to 1.5 meq/L. The trend in dissolved color reduction with increased coagulant dose was similar for each source water and coagulant combination. A coagulant dose of 1 meq/L reduced the color by approximately 50 percent. Total reduction in DOC using 2 meq/L of coagulant was between 25 and 42 percent indicating that the concentration and nature of organic matter appears to require a high dose of coagulant to achieve settleable particle formation. Based on the overall results a dose of 1 to 1.5 meq/L of coagulant was selected and used in subsequent testing.

5.2 Polymer Screening for Selection of Polymer Product(s).

The results from polymer screening and selection testing are presented in this section. The NEAA and SSTA waters were dosed with 1meq/L of either alum or ferric chloride and then with one of the polymers selected for screening at a dose of either 0.25 or 0.5 mg/L active ingredient. Three emulsion polyacrylamide polymers were selected for testing: Cytec's Superfloc flocculants A-1849RS; A-1883RS, and N-1986. These polymers are NSF International approved for drinking water. The A-1849RS has a 3percent anionic charge and a medium molecular weight. The A-1883RS has a 30percent anionic charge and high molecular weight. The N-1986 polymer has a 0percent charge or nonionic and a medium molecular weight. Consistent with previous jar testing, after the polymer was added the samples were rapid mixed for 15 seconds and then flocculated for 20 minutes. After the flocculation period ended, the samples were allowed to settle. During the settling period aliquots were collected from a depth of 10 cm below the initial liquid surface at times 1, 2, 5, and 10 minutes for turbidity measurement. The sample collection times correspond to hydraulic surface loading rates (SLR) of 2.5, 1.2, 0.5, and 0.25 gpm/sft. Process pH was held within the range of 6.5 to 7.0 SU for alum and 7.0 to 8.0 SU for ferric chloride.

The results of turbidity measurement with respect to SLR when using alum as the coagulant on NEAA waters are presented in Figure 9. The N-1986 polymer at a dose of 0.5 mg/L performed the best on the NEAA water. The A-1849 also performed well at a dose of 0.5 mg/L and enhanced the settling of particles at a dose of 0.25 mg/L. The 30percent charge and higher molecular weight A-1883 polymer did not perform well under these conditions.

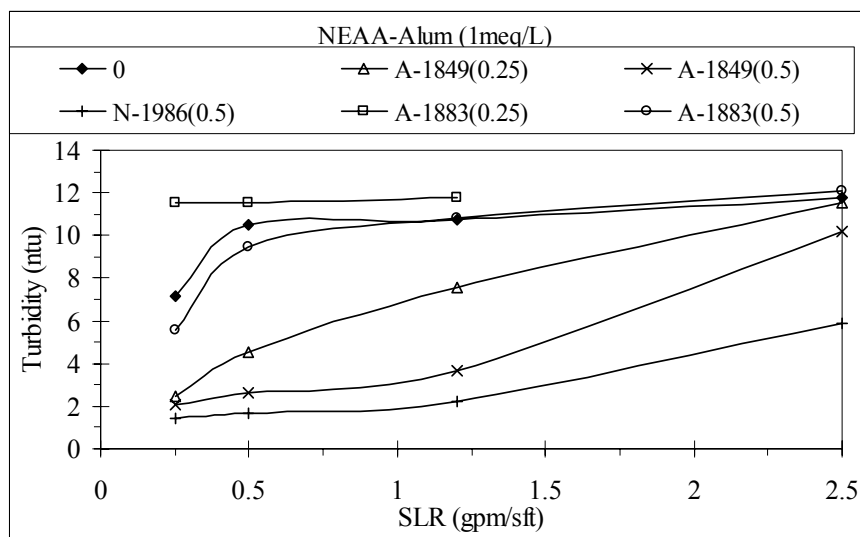


Figure 9 Polymer Selection - Alum Treatment of NEAA Water

The turbidity measured for the NEAA water treated with ferric chloride is presented in Figure 10. The A-1849 polymer at a dose of 0.5 mg/L performed the best. The ferric chloride dose was increased to 1.5 meq/L with the same 0.5 mg/L dose of A-1849 and performed as well, indicating there is flexibility with dose of coagulant used.

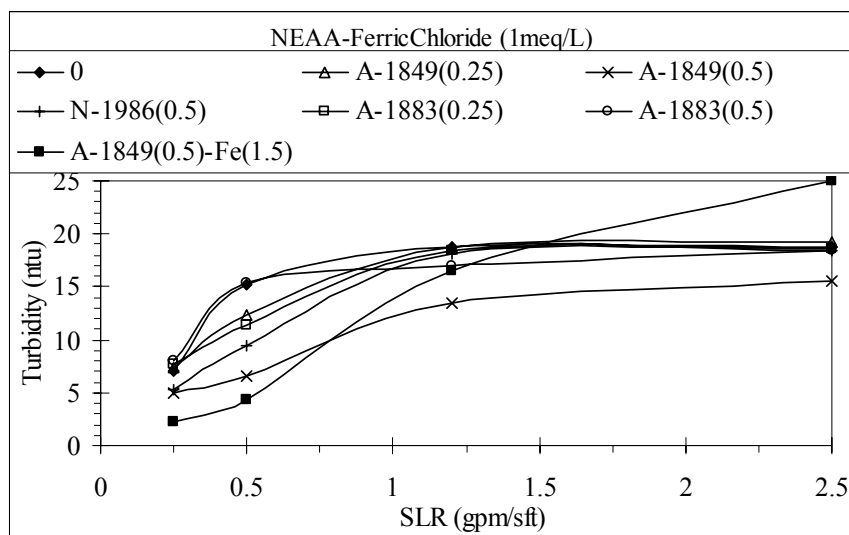


Figure 10 Polymer Selection - Ferric Chloride Treatment of NEAA Water

The turbidity measured for SSTA water treated with alum is presented in Figure 11. The A-1849 polymer at a dose of 0.5 mg/L performed the best. The test was repeated with similar results and is shown in the Figure 11 as "A-1849(0.5)Dup".

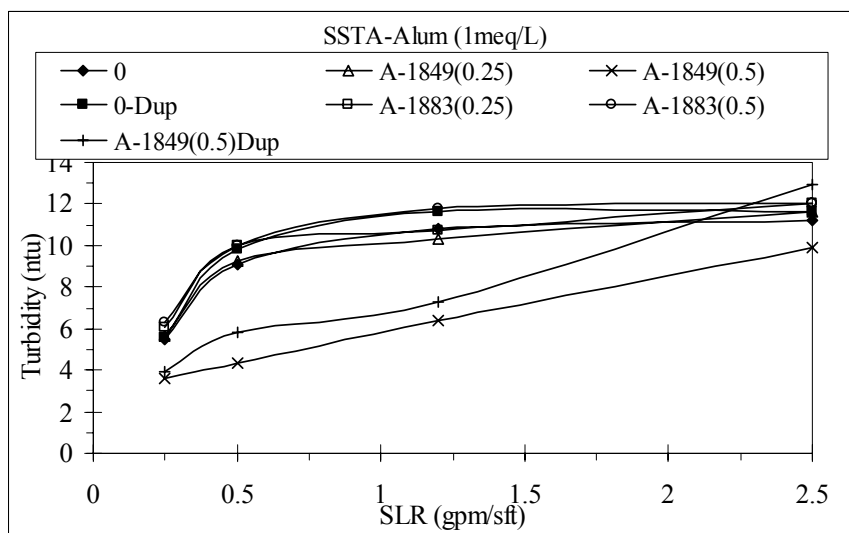


Figure 11 Polymer Selection - Alum Treatment of SSTA Water

The alum dose was increased to 1.5 meq/L with the same 0.5 mg/L dose of A-1849 and the N-1986 polymer at a dose of 0.5 mg/L. The results are compared with the lower alum dose of 1.0 meq/L and the A-1849 polymer in Figure 12. The N-1986 polymer performed adequately at the 0.5 gpm/sft SLR. The A-1849 performed the best with excellent performance shown with the higher dose of alum. This again indicates there is flexibility in usage of a 0.5 mg/L dose of A-1849 with varying coagulant dose in this range.

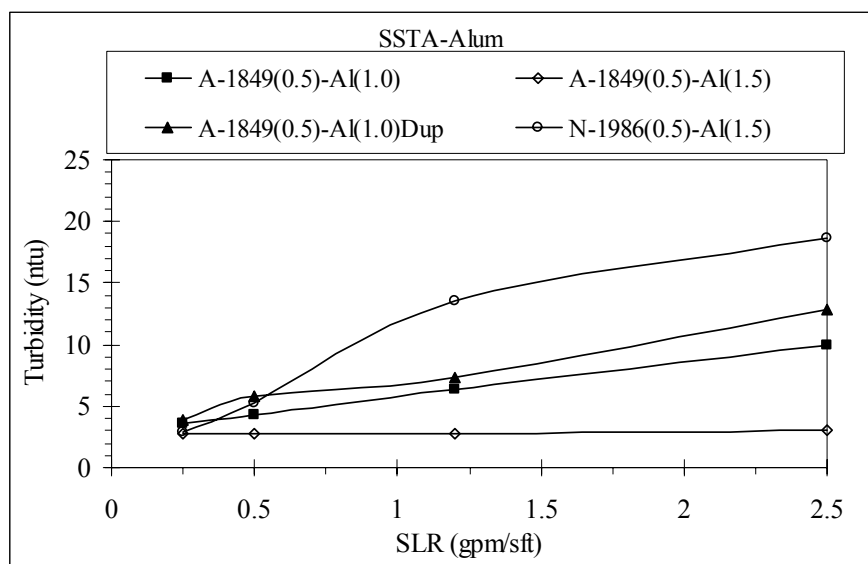


Figure 12 Polymer Selection - Alum Treatment of SSTA Water

The turbidity measured for SSTA water treated with ferric chloride is presented in Figure 13. The 1 minutes sample time corresponding to the 2.5 gpm/sft SLR was not recorded. The A-1849 polymer at a dose of 0.5 mg/L performed the best. However, the overall performance between coagulant and polymer was not considered adequate. The 1 meq/L ferric chloride and 0.5 mg/L A-1849 polymer combination was tested again and produced a similar result at the 1.2 gpm/sft SLR but improved significantly at the 0.5 gpm/sft SLR. It is identified as "A-1849(0.5)Dup" in Figure 13.

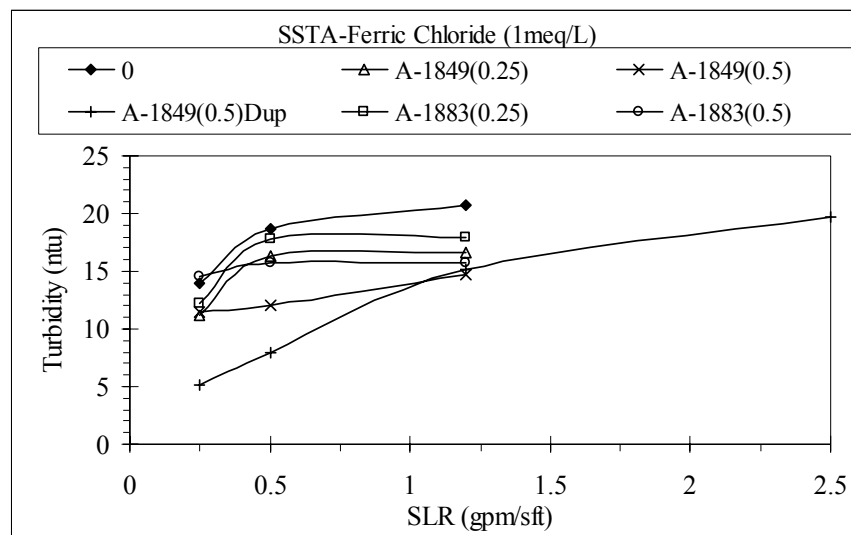


Figure 13 Polymer Selection - Ferric Chloride Treatment of SSTA Water

To determine if increased dose would improve settling characteristics, the ferric chloride dose was increased to 1.5 meq/L with the same 0.5 mg/L dose of A-1849 polymer. Another sample was tested with a ferric chloride dose of 1.5 meq/L and the N-1986 polymer at a dose of 0.5 mg/L. The results were compared with the lower ferric chloride dose of 1.0 meq/L and the A-1849 polymer in Figure 14. The N-1986 polymer and A-1849 both showed excellent floc characteristics and settling performance with the higher dose of ferric chloride. This and the SSTA results using alum treatment indicate that settling performance for the SSTA water is enhanced with the higher dose of coagulant, and is less sensitive to polymer type or dose.

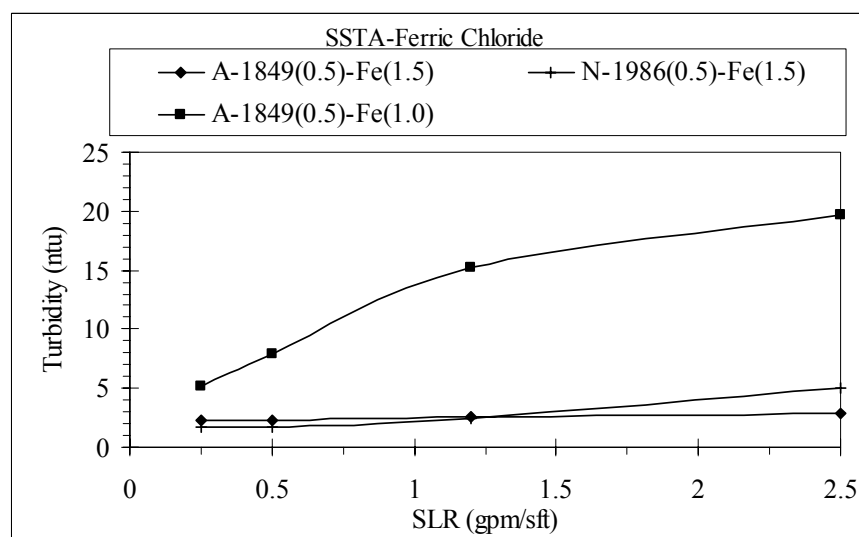


Figure 14 Polymer Selection - Ferric Chloride Treatment of SSTA Water

The results of the polymer selection testing determined that the A-1849 anionic polymer at a dose of 0.5 mg/L promoted the best overall particle agglomeration and settling, and was thus selected for further testing. The nonionic N-1986 polymer showed adequate performance and should be a candidate for further testing should charge build-up during sludge blank formation occur in subsequent tests and future pilot studies. The higher molecular weight and 30percent charge anionic A-1883 polymer did not perform adequately and was not selected for further testing.

5.3 Polymer Dosage Optimization.

The results from polymer dose optimization tests are presented in this section. The tests consisted of holding the preselected coagulant dose for each water source constant and varying the dose of polymer. Based on the previous section the A-1849RS polymer with a 3percent anionic charge and a medium molecular weight was selected for polymer dose optimization. Based on the results of the previous two sections an alum dose of 1 meq/L was selected for use in treating the NEAA water and a dose of 1.5 meq/L was selected for the SSTA water. A ferric chloride dose of 1.5 meq/L was selected for use in treating both the NEAA and SSTA waters. Consistent with previous jar testing, after the polymer was added the samples were rapid mixed for 15 seconds and then flocculated for 20 minutes. After the flocculation period ended, the samples were allowed to settle during which aliquots were collected from a depth of 10 cm at times 1, 2, 5, and 10 minutes for turbidity measurement. The sample collection times correspond to SLRs of 2.5, 1.2, 0.5, and 0.25 gpm/sft, respectively. Process pH was held within the range of 6.5 to 7.0 for alum and 7.0 to 8.0 for ferric chloride. Fresh NEAA and SSTA water samples were collected the previous day for use in the polymer dosage optimization tests.

The alum coagulation treatment of NEAA water was evaluated with four doses of A-1849 polymer at concentrations of 0.1, 0.3, 0.5 and 0.7 mg/L as active ingredient. An alum dose of 1 meq/L selected from previous results was used during the testing. A polymer dose of 0.7 mg/L performed the best as shown in Figure 15. The polymer dose of 0.5 mg/L performed almost as well producing settling results that were not significantly different from the higher dose and was therefore selected for the subsequent solids contact simulation testing.

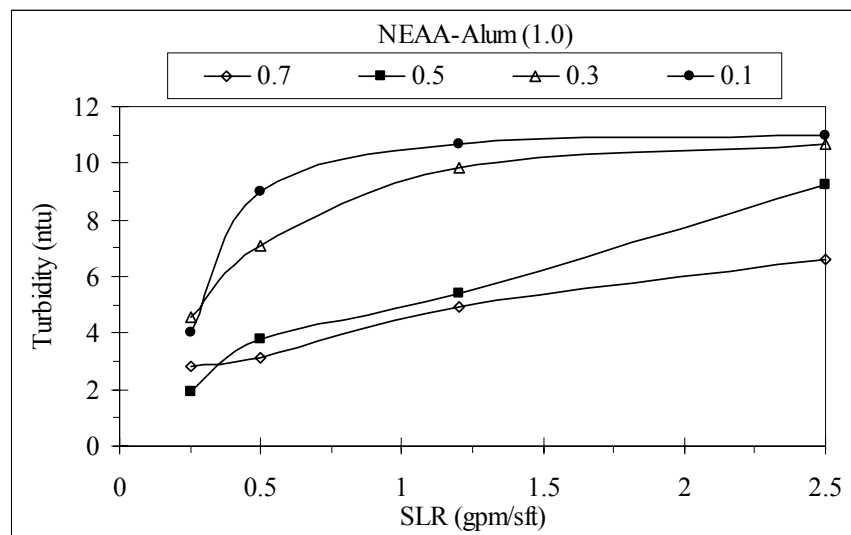


Figure 15 Polymer Dosage Optimization - Alum Treatment of NEAA Water

Ferric Chloride treatment of NEAA water was evaluated with three doses of A-1849 polymer at concentrations of 0.5, 0.6 and 0.7 mg/L as active ingredient. A ferric chloride dose of 1.5 meq/L selected from previous results was used during the testing. A polymer dose of 0.7 mg/L performed the best throughout the SLR range evaluated as shown in Figure 16. The polymer doses of 0.5 and 0.6 mg/L performed almost as well producing settling results at SLRs below 1.2 gpm/ft² that were not significantly different from the higher dose. A polymer dose of 0.5 mg/L was thus selected for the subsequent solids contact simulation testing.

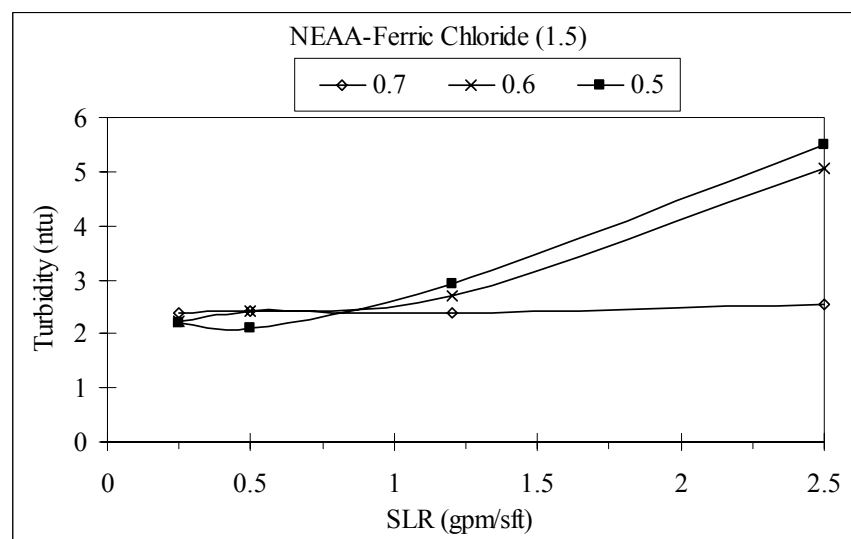


Figure 16 Polymer Dosage Optimization - Ferric Chloride Treatment of NEAA Water

Alum treatment of SSTA water was evaluated with three doses of A-1849 polymer at concentrations of 0.1, 0.3 and 0.5 mg/L as active ingredient. An alum dose of 1.5 meq/L was selected from previous results and used during the testing. A polymer dose of 0.5 mg/L performed the best as shown in Figure 17. The polymer doses of 0.1 and 0.3 mg/L did not perform as well. A polymer dose of 0.5 mg/L was selected for the subsequent solids contact simulation testing.

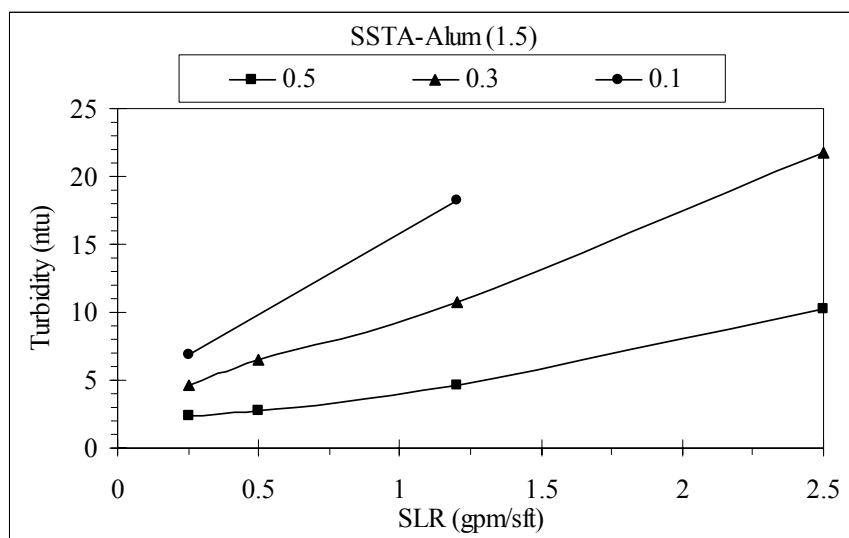


Figure 17 Polymer Dosage Optimization - Alum Treatment of SSTA Water

Ferric Chloride treatment of SSTA water was evaluated with four doses of A-1849 polymer at concentrations of 0.1, 0.5, 0.6 and 0.7 mg/L as active ingredient. A ferric chloride dose of 1.5 meq/L selected from previous results was used during the testing. Polymer doses of 0.6 and 0.7 mg/L performed the best and equally well as shown in Figure 18. The polymer dose of 0.5 mg/L performed almost as well at the SLR of 0.5 gpm/ft². A polymer dose of 0.1 mg/L did not perform well except at the low SLR of 0.25 gpm/ft². A polymer dose of 0.6 mg/L was selected for the subsequent solids contact simulation testing.

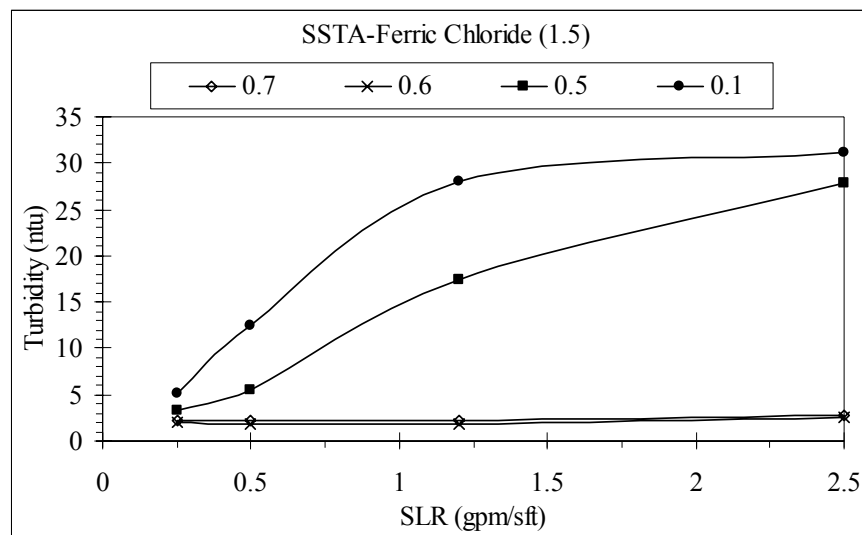


Figure 18 Polymer Dosage Optimization - Ferric Chloride Treatment of SSTA Water

Water quality analyses conducted on the raw source and treated waters from selected coagulant and polymer dose combinations are presented in Table 2. The treated water samples were collected after a settling time of 10 minutes. The samples were split between the SFWMD Laboratory and PPB Environmental Labs Inc. for total phosphorus and dissolved total phosphorus analysis. In general, the PPB lab results are consistently higher than the SFWMD with the highest differences associated with total phosphorus. The difference between the total dissolved phosphorus of the two laboratories was significantly less ranging from 2 to 7 ug/L, except for the NEAA water treated with ferric chloride and a polymer dose of 0.5 mg/L. Both the NEAA and SSTA source waters had low levels of total dissolved phosphorus. As seen during the coagulant optimization tests the total dissolved phosphorus was decreased in waters treated with alum to near or below the 10 ug/L level. The results from waters treated with ferric chloride show an increase in total dissolved phosphorus. The total dissolved phosphorus analysis on the chemicals used during the testing, at concentration of 1meq/L are also presented in Table 2. The ferric chloride showed an 11 ug/L total dissolved phosphorus analysis at a dose of 1 meq/L. This could indicate that the ferric chloride was either introducing phosphorus to the jar test or interfered with the analytical method. The dissolved ortho-phosphorus was measured near the detection limit 3 to 6 ug/L. The aluminum concentration increased in the alum treated water by 90 to 152 ug/L Al. The NEAA water treated with ferric chloride decreased in iron concentration while the SSTA increased in concentration. The color of the NEAA was reduced by approximately 57 percent while the SSTA treated water was reduced by 50 to 65 percent. The coagulation process removed approximately 30 percent of the dissolved organic carbon.

Table 2 Polymer Dosage Optimization - Water Quality

Sample Description	SFWMD		PPB Lab						
	Total P µg/l	Total Dis.- P µg/l	Total P µg/l	Total Dis.- P µg/l	Dis. Ortho-P µg/l	Dis. Al µg/l	Dis. Fe µg/l	Dis. Color Cpu	Dis. Organic. C mg/l
NEAA - Raw	20	12	62	14	4	332	23	172	29.3
SSTA - Raw	19	8	34	13	4	329	12	200	35
NEAA, 1.5 Fe, 0.5 Polymer	20	13	33	20	<2		12	74	19.1
NEAA, 1.5 Fe, 0.6 Polymer	21	14	34	28	6		21	75	19
NEAA, 1.0 Al, 0.7 Polymer	10	6	47	11	4	484		76	19.8
NEAA, 1.0 Al, 0.5 Polymer	10	6	37	9	4	447		70	22.7
SSTA, 1.5 Fe, 0.7 Polymer	21	15	32	19	4		29	103	26.2
SSTA, 1.5 Fe, 0.6 Polymer	23	16	38	22	4		18	102	25.6
SSTA, 1.5 Al, 0.5 Polymer	11	5	15	9	4	419		70	24
SSTA, 1.5 Al, 0.3 Polymer	9	5	16	8	3	432		70	23.8
FeCl3 (1 meq/L)	11								
Alum (1 meq/L)	<3								
NaOH (1 meq/L)	<3								

*Coagulant dose in meq/L, polymer dose in mg/L active ingredient

**Dis. Filtered @ 0.45 um

The results of the polymer dose optimization testing determined that the A-1849 anionic polymer at a dose of 0.5 to 0.6 mg/L produced acceptable turbidity reduction within the practical range of SLRs that are anticipated to be employed in the field.. This dose range of polymer was selected for the subsequent solids contact simulation testing. The water quality analysis indicated that alum doses of 1.0 meq/L for the NEAA and 1.5 meq/L of the SSTA could reduce total dissolved phosphorus below 10 ug/L. The alum treatment increased dissolved aluminum concentrations by 90 to 150 ug/L Al. Increasing the alum dosage by 0.5 meq/L would be expected to leave the treated water aluminum concentration at approximately the raw water background concentration. Results of ferric chloride treatment for phosphorus reduction were inconclusive. Residual iron in the ferric chloride treated waters remained near background levels with concentrations of 0.12 to 0.29 ug/L dissolved iron. Dissolved color and organic carbon were reduced by 30 to 65percent.

5.4 Solids Contact Simulation.

The results from solids contact simulation testing are presented in this section. The tests consisted of treating a sequential set of jars holding the selected coagulant and polymer doses for each water source constant. Consistent with previous jar testing, after the polymer was added the samples were rapid mixed for 15 seconds and then flocculated for 20 minutes. After approximately 20 minutes of settling the jar was decanted leaving 400 ml of the settled solids and water. The next jar in the sequence treated 1600 ml of the source water and after rapid mix

the 400 ml of solids and liquid from the previous jar was introduced at the beginning of the flocculation time period. The original testing protocol called for a sequence of 12 jars to simulate a solids retention time of 24 hours. However, there was only sufficient water from a single grab-sampling event to treat 10 jars in sequence during actual testing. The simulated solids retention time for actual testing was thus 20 hours.

Based on the previous testing the A-1849RS polymer was selected at a dose of 0.5 mg/L for treatment of NEAA water with both alum and ferric chloride. For the SSTA water the A-1849RS polymer was dosed at 0.5 mg/L with the alum and 0.6 mg/L with the ferric chloride. An alum or ferric chloride dose of 1.5 meq/L was selected for use in treating both the NEAA and SSTA waters. After the flocculation period ended for jars 4, 8 and 10 in the sequence, sample aliquots were collected during settling from a depth of 10 cm below the initial liquid surface at times 1, 2, 5, and 10 minutes for turbidity measurement. The sample collection times correspond to hydraulic SLRs of 2.5, 1.2, 0.5, and 0.25 gpm/sft. Process pH was maintained within the range of 6.5 to 7.0 for alum and 7.0 to 8.0 for ferric chloride. The ferric chloride required 1 meq/L of sodium hydroxide added immediately prior to the coagulant to maintain the target pH. The alum treatment did not require chemical addition for control of pH in the specified range.

The results of turbidity measurements recorded after batches 4, 8 and 10 in each sequence of the treated waters is presented in Figures 19 through 22. In general, there were no adverse affects on particle formation or settling characteristics observed with the increase in solids. The initial turbidity measured at the 2.5 gpm/ft² SLR increased with increasing solids concentration (batches). However, the turbidity measurement between batches converged rapidly at the 1.2 gpm/ft² SLR and batch 10 with the highest solids produced the same or lowest turbidity at the 0.25 gpm/ft² SLR. The turbidity measurements indicate that the increased solids enhanced the clarification characteristics through a “sweep floc” effect and charge build-up from increased polymer mass was not experienced.

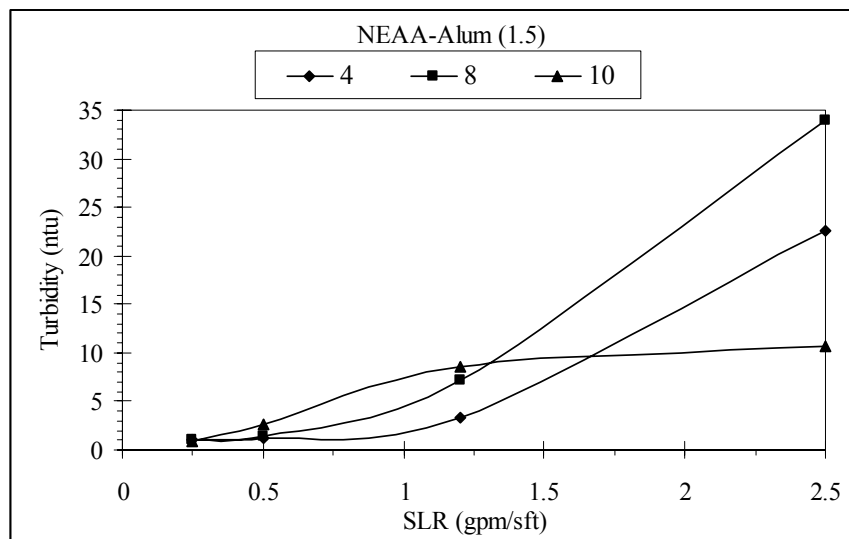


Figure 19 Solids Contact Simulation - Alum Treatment of NEAA Water

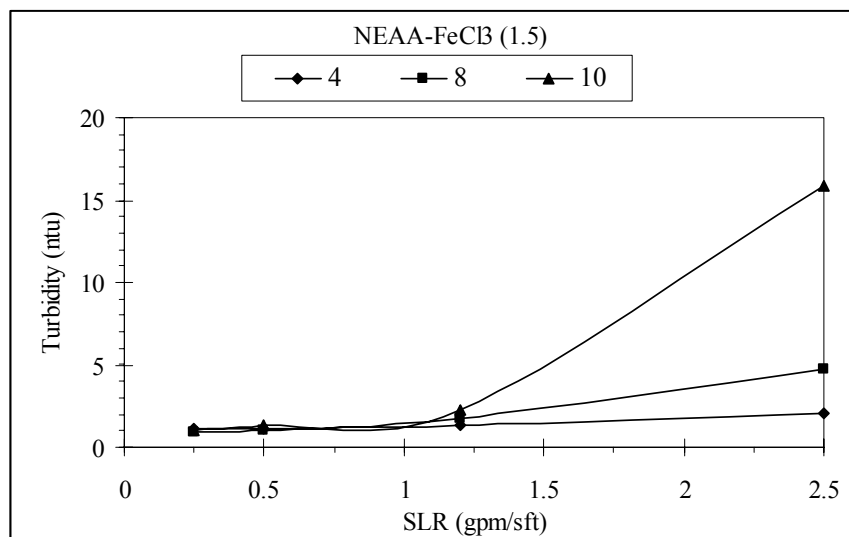


Figure 20 Solids Contact Simulation - Ferric Chloride Treatment of NEAA Water

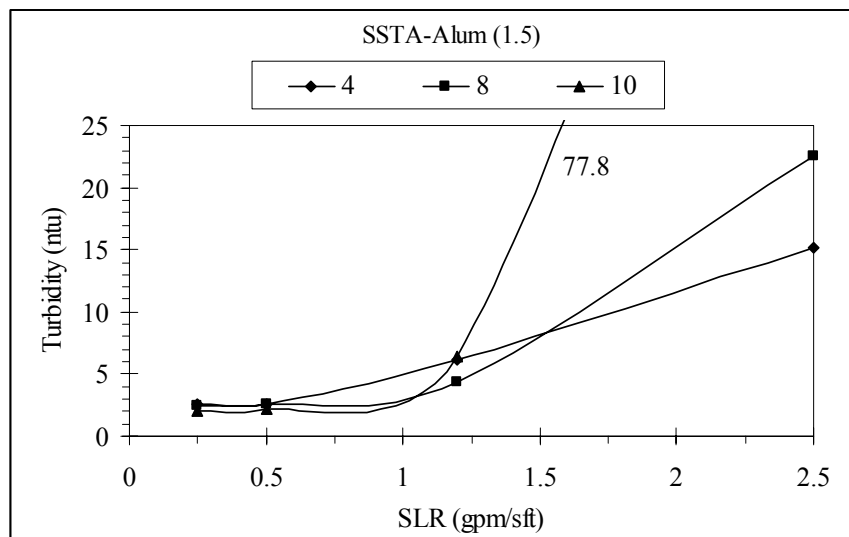


Figure 21 Solids Contact Simulation - Alum Treatment of SSTA Water

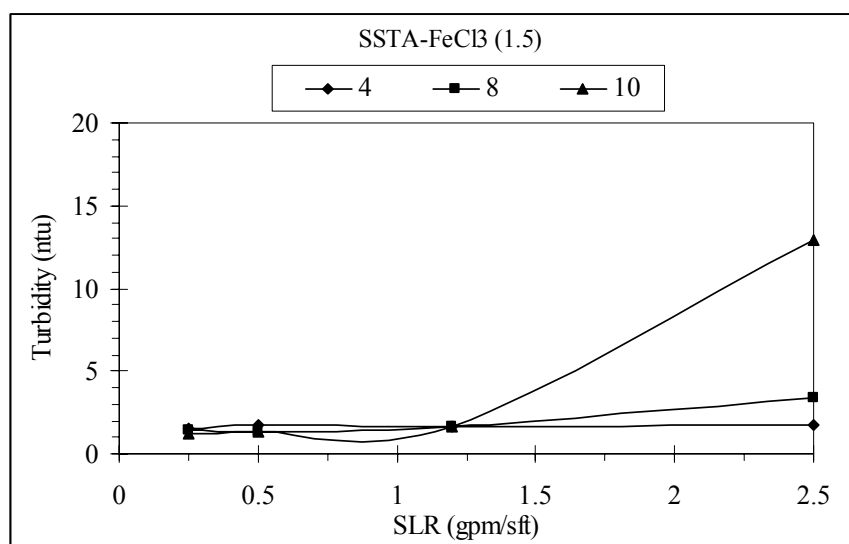


Figure 22 Solids Contact Simulation - Ferric Chloride Treatment of SSTA Water

The water quality analyses performed on the raw source waters and batch 10 samples for each test, the finished waters for each treatment of the solids contact simulation tests, are presented in Table 3. The reported total phosphorus concentration increased in the finished waters of all tests except the SSTA water with alum treatment. However, alum treatment of both waters reduced the reported total dissolved phosphorus below 10 ug/L. Both waters treated with ferric chloride, consistent with proceeding testing results increased the reported total dissolved phosphorus in the treated water. The ferric chloride treatment reduced background aluminum by approximately 24 ug/L Al. The alum treatment increased the background aluminum by 54 ug/L (NEAA) and 100

ug/L Al (SSTA). Background iron was reduced to detection level by alum treatment. Background iron was reduced 50 percent with ferric chloride treatment of the NEAA water. The ferric chloride treatment of the SSTA water approximately doubled the background iron to 40 ug/L Fe. The dissolved color and organic carbon of the treated waters was reduced by 50 to 78 percent and 18 to 42 percent, respectively. The alum treatment reduced dissolved color and organic carbon greater than the ferric chloride treatment.

Table 3 Solids Contact Simulation - Water Quality

Sample Description	Total P	Total Dis.-P	Dis. Ortho-P	Dis. Al	Dis. Fe	Dis. Color	Dis. Organic C
	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(cpu)	(mg/L)
NEAA – Raw	36	12	3	323	24	153	28
SSTA – Raw	32	14	4	322	26	188	38
NEAA, 1.5 Fe, 0.5 Polymer	55	22	<2	300	12	61	23
SSTA, 1.5 Fe, 0.6 Polymer	65	24	<2	297	40	87	29
NEAA, 1.5 Al, 0.5 Polymer	42	8	<2	377	<4	34	18
SSTA, 1.5 Al, 0.5 Polymer	19	8	<2	423	<4	55	22

Coagulant dose in meq/L, polymer dose in mg/L active ingredient

Dis. Filtered @ 0.45 µm,

The total solids produced during the solids contact simulation testing is presented in Table 4. The finished solids volume was measured and sampled for total suspended solids (TSS) measurement. TSS was measured two ways in the laboratory. One was by directly weighing a filter aliquot after drying and the second was by subtracting a total dissolved solids measurement from a total solids measurement. Table 4 presents the TSS results for both of these methods in addition to the calculated concentration based on stoichiometry and measured natural solids reduction. The volume of sludge produced after the 10 sequential batch tests was approximately 200 ml after 30 minutes of thickening for each water and chemical treatment. The concentration of TSS in the thickened sludge ranged from 3600 to 6400 mg/L, depending on the method and source. In general, the TSS measured by difference was lower than the directly measured concentration, which was lower than the stoichiometrically calculated measurement. However, the three methods compare fairly well with each other. The two measured values were averaged to provide the reported solids production for each source water/coagulant combination. Waters treated with iron coagulant produced 63 to 71 mg of solids per liter of water treated. Alum treated waters produced significantly lower sludge quantities, ranging from 49 to 54 mg of TSS per liter of water treated..

Table 4 Solids Contact Simulation - Solids Production

	Solids Concentration in 200ml				Solids Production			
Sample Description	Sludge	Differ.	Direct	Stoich.	Differ.	Direct	Stoich.	Avg
	Volume	TSS	TSS	TSS	TSS	TSS	TSS	TSS
	(ml)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
NEAA, 1.5 Fe, 0.5 Polymer	200	5151	5121	6101	63	62	74	63
SSTA, 1.5 Fe, 0.6 Polymer	200	5230	6286	6437	64	77	79	71
NEAA, 1.5 Al, 0.5 Polymer	200	4089	4698	5023	50	57	61	54
SSTA, 1.5 Al, 0.5 Polymer	200	3620	4371	5515	44	53	67	49

Coagulant doses in meq/L, polymer doses in mg/L active ingredient.

Differ. = Difference between measured total solids and total dissolved solids.

Stoich. = Calculated based on Stoichiometry and natural solids reduction.

In general, there were no adverse affects on particle formation or settling characteristics observed with the increase in solids. The turbidity measurement between batches converged rapidly at the 1.2 gpm/ft² SLR and batch 10 with the highest solids produced the same or lowest turbidity at the 0.25 gpm/ft² SLR. The total phosphorus concentration increased in the finished water of all treated waters except for the SSTA water with alum treatment, indicating some type of experimental contamination, concentrating effect onto solids, or analytical interference. Alum treatment of both waters reduced the reported total dissolved phosphorus below 10 ug/L P. Both waters treated with ferric chloride, consistent with proceeding testing results increased the reported total dissolved phosphorus in the treated water. . The alum treatment increased the background aluminum by 54 and 100 ug/L Al. Ferric chloride treatment decreased background iron by 50percent in the NEAA water but double the concentration in the SSTA water. The residual solids measurements determined that a dose of 1.5 meq/L would produce an average of 51 mg/L TSS using alum and 67 mg/L TSS using ferric chloride. After 30 minutes of thickening the percent solids of the residuals averaged 0.4 percent for alum and 0.5 percent for ferric chloride.

4.5 Sludge Storage Evaluation

At the time of this writing, the sludge storage evaluation was in progress and no preliminary testing results were available. This technical memorandum will be updated and redistributed with sludge storage evaluation results at the completion of that testing.

Quality Control and Assurance Results

A summary of blanks, duplicates (precision), and matrix spikes (accuracy) produced during the course of the laboratory prescreening for chemical selection is presented in the following section. This quality control and assurance (QA/QC) section contains results obtained from samples submitted by the investigators and internal laboratory QA/QC supplied by the individual laboratories as part of their report of analytical results. The primary tools used to control quality in the laboratory are the evaluation of experimental blanks, precision and accuracy. Blanks are used to reveal experimental contamination of sample handling. Precision is used to reveal experimental reproducibility and the accuracy is used to compare an experimentally determined value with an accepted true value. The QA/QC section is divided into subsections titled; Field Blanks, Precision, and Accuracy.

5.5 Field Blanks

A summary of the field blanks is presented in this section. Field blanks were samples of de-ionized water aliquots that were carried through the same handling procedure as experimentally derived samples for a specific analysis. For instance, a blank for total dissolved phosphorus consisted of de-ionized water that had been filtered using the peristaltic pump and 0.45 micron filter and preserved with sulfuric acid before submittal to the laboratory along with the other samples that day for analysis.

The field blanks for phosphorus and general water quality analysis are presented in Tables 5 and 6. The results of phosphorus field blanks are at or near detection limits except for total phosphorus analysis. The limited results show the blank results from the contract lab were higher, averaging 7 ug/L P, than the district lab's results at the detection limit. Results presented with a "<" (less than sign) represent a detection limit shift from the presented laboratory standard due to an analytical sample volume change. The general water quality parameters presented in Table 6 show that almost all were below the detection limit.

The field blanks indicate that the sample handling techniques were sufficient to limit sample contamination.

Table 5 Field Blank Phosphorus Analysis

Sample Date	SFWMD Results			PPB Environmental Labs Results		
	Total P µg/l	Total Dis.-P µg/l	Dis. Ortho-P µg/l	Total P µg/l	Total Dis.-P µg/l	Dis. Ortho-P µg/l
3/9/99	4	3	2	6	<3	<3
3/9/99		5				
3/9/99		3				
3/9/99		3				
3/11/99	2	4	2	8		
3/12/99				7	3	<2
Max	4	5	2	8	3	3
Min	2	3	2	6	3	2
Avg	3	3.6	2	7	3	2.5
Detect. Limit	3.6	3.6	3.6	3	3	2

Table 6 Field Blank General Water Quality Analysis

Sample Date	Dis. Al µg/l	Diss. Fe µg/l	Dis. Color cpu	Dis. Org. C mg/l	TSS mg/l
3/9/99	5	<2	<10	<2	<10
3/9/99	10.2		<5	<2	
3/9/99		<2	<5	<2	
3/9/99	<5		<5	<2	
3/9/99		<2			
3/11/99	<11	<4	<5	3.96	
3/12/99	<11	<4	<5	5.34	
Max	11	4	10	5.34	
Min	5	2	5	2	
Avg	8.44	2.8	5.83	2.88	
Detect. Limit	5	2	5	2	2

5.6 Precision

During the chemical analyses, duplicating a previously measured sample assesses precision. Laboratory duplicates are samples selected by the laboratory internally to assess the analytical precision. Field duplicates consisted of two aliquots of the same sample submitted by the investigators with different sample identification. Field duplicates minimize the effect of analyst bias on precision. In addition to submitting duplicate samples, several samples were further split between the District and the contract lab. In essence, certain samples were blindly analyzed four times. An assessment of precision is the difference between the two readings divided by the

average and reported as a relative percent difference (RPD). The following equation is used to quantify RPD.

$$\text{percent RPD} = \frac{\text{Reading1} - \text{Reading2}}{\text{AverageReading}} \times 100$$

Table 7 and 8 present the field duplicates and split samples analyzed for phosphorus by the District and contract labs. In general both laboratories show very good precision. The district's analysis of total phosphorus produced precision below detectable limits and the contract lab difference was less than 4 ug/L P, except for one sample. The total dissolved phosphorus results produced by the contract lab where consistently higher than the district' lab by 8 to 19 ug/L

Table 7 Field Duplicates and Split Samples - Total Phosphorus

Sample	Sample Description	SFWMD - Total P			PPB Env. Labs - Total P		
Date		Reading 1	Reading 2	RPD	Reading 1	Reading 2	RPD
		µg/l	µg/l	%	µg/l	µg/l	%
3/9/99	NEAA Raw Dup.	26	26	<	34	35	2.9
3/9/99	SSTA Raw Dup.	21	21	<	34	36	5.7
3/11/99	NEAA-Fe1 Dup.	20	20	<	29	33	12.9
3/12/99	NEAA-Fe Dup.				85	55	42.9
	Maximum Value						42.9
	Minimum Value						2.9
	Average Value						7.2
	Standard Deviation						5.2
	Detection Limits	3.6	3.6		3	3	

The total dissolved phosphorus results show that the District's lab produced very good precision with differences below detection to 2 ug/L P. The contract laboratory produced similar results except for one sample with a difference of 7 ug/L P. The contract lab consistently produced higher concentrations than the district by 7 ug/L.

Table 8 Field Duplicates and Split Samples - Total Dissolved Phosphorus

Sample Date	Sample Description	SFWMD - Total Dis. P			PPB Env. Labs - Total Dis. P		
		Reading 1 µg/l	Reading 2 µg/l	RPD %	Reading 1 µg/l	Reading 2 µg/l	RPD %
3/9/99	NEAA Raw Dup.	16	15	6.5	17	17	<
3/9/99	SSTA RawDup.	10	12	18.2	19	12	45.2
3/9/99	NEAA-All Dup.	7	6	15.4			
3/9/99	SSTA-All.5 Dup.	5	5	<			
3/9/99	NEAA-Fe1 Dup.	14	14	<			
3/9/99	SSTA-Fe0.75 Dup.						
3/11/99	NEAA-Fe1 Dup.	13	13	<	19	20	5.1
3/12/99	NEAA-Fe Dup.				23	22	4.4
	Maximum Value			18.2			45.2
	Minimum Value			<			<
	Average Value			6.7			16.8
	Standard Deviation			8.3			24.7
	Detection Limits	3.6	3.6		3	3	

The results and precision of dissolved ortho-phosphorus analysis produced by both laboratories were similar. Both laboratories showed excellent precision, even though the samples analyzed contained ortho-P at concentrations very near to the detection limit. The dissolved ortho-phosphorus precision results are presented in Table 9.

Table 9 Field Duplicates and Split Samples - Dissolved Ortho Phosphorus

Sample Date	Sample Description	SFWMD - Dis. Ortho-P			PPB Env. Labs - Dis. Ortho-P		
		Reading 1 µg/l	Reading 2 µg/l	RPD %	Reading 1 µg/l	Reading 2 µg/l	RPD %
3/9/99	NEAA Raw Dup.	5	5	<	5	5	<
3/9/99	SSTA Raw Dup.	5	5	<	3	4	28.6
3/11/99	NEAA-Fe1 Dup.	NR	NR		<2	4	66.7
3/12/99	NEAA Fe Dup.				<2	<2	<
	Maximum Value			<			66.7
	Minimum Value			<			<
	Average Value			<			31.8
	Standard Deviation			<			33.5
	Detection Limits	3.6	3.6		3	3	

The precision results from the analysis of field duplicates for dissolved aluminum and iron are presented in Table 10 and for dissolved color and organic carbon in Table 11. In general the precision is good for all the parameters. Dissolved iron recorded the highest RPD which is directly effected by the lower magnitude of the values. That is, a small difference in a low concentration produces a high RPD. The results indicate that at the levels measured there was a

higher variability for iron and organic carbon. However, the relative difference for these particular parameters at the low levels achieved by the treatment is not considered a major concern for this testing evolution.

Table 10 Field Duplicates and Split Samples - Dissolved Aluminum and Iron

Sample Date	Sample Description	Dissolved Al			Dissolved Fe		
		Reading 1 µg/l	Reading 2 µg/l	RPD %	Reading 1 µg/l	Reading 2 µg/l	RPD %
3/9/99	NEAA Raw Dup.	363	364	0.3	33	16	69.4
3/9/99	SSTA Raw Dup.	378	372	1.6	13	6	73.7
3/9/99	NEAA-Al1Dup.	350	370	5.6			
3/9/99	SSTA-Fe1.5 Dup.	394	374	5.2			
3/9/99	NEAA-Fe1 Dup.				16	10	46.2
3/9/99	SSTA-Fe0.75 Dup.				94	90	4.3
3/11/99	NEAA-Fe1 Dup.				12	10	18.2
3/12/99	NEAA-Fe Dup.	300	298	0.7	12	6	66.7
	Maximum Value			5.6			73.7
	Minimum Value			0.3			4.3
	Average Value			3.2			42.4
	Standard Deviation			2.6			30.6
	Detection Limits	5	5		2	2	

Table 11 Field Duplicates - Dissolved Color and Organic Carbon

Sample Date	Sample Description	Dissolved Color			Dissolved Organic Carbon		
		Reading 1 cpu	Reading 2 Cpu	RPD %	Reading 1 mg/l	Reading 2 mg/l	RPD %
3/9/99	NEAA Raw Dup.	150	153	2.0	24.3	24.6	1.2
3/9/99	SSTA Raw Dup.	192	186	3.2	32.1	32.3	0.6
3/9/99	NEAA-Al1Dup.	56	56	0.0	20.7	17.1	19.0
3/9/99	SSTA-Fe1.5 Dup.	63	65	3.1	26	21.1	20.8
3/9/99	NEAA-Fe1 Dup.	67	70	4.4	21.8	20	8.6
3/9/99	SSTA-Fe0.75 Dup.						
3/11/99	NEAA-Fe1 Dup.	74	73	1.4	19.1	20.4	6.6
3/12/99	NEAA-Fe Dup.	61	59	3.3	23.4	18	26.1
	Maximum Value			4.4			26.1
	Minimum Value			0.0			0.6
	Average Value			2.3			9.5
	Standard Deviation			1.6			8.7
	Detection Limits	5	5		2	2	

The experimental duplication performed on the NEAA and SSTA waters with ferric chloride treatment is presented below. The jar tests were repeated because the first set conducted on 3/9/99 produced higher than expected results for total dissolved phosphorus. The differences between the two sets are:

1. The first set was pH adjusted with 50percent sodium hydroxide and the second used reagent grade sodium hydroxide.
2. The source water samples were from the same batch collected 3/8/99, however it was refrigerated at 4 °C for three days and warmed overnight at room temperature before the second test was conducted on 3/12/99.
3. The analysis of the first set was conducted by the District's lab and the contract lab conducted the second analysis.

In general, both samples show concentrations higher than anticipated with total dissolved phosphorus either stable or increasing with increasing ferric chloride dose. The sodium hydroxide does not appear to be a source of phosphorus. Consistent with earlier split sample trends, the contract lab values are consistently greater than the district's analysis.

Table 12 Experimental Duplication

Dose	Dissolved Total Phosphorus (ug/L P)			
(meq/L)	NEAA-3/9/99	NEAA-3/12/99	SSTA-3/9/99	SSTA-3/12/99
0	16	12	11	14
0.25	10		11	
0.5	12	18	12	18
0.75	12	19	14	20
1	14	18	17	20
1.5	14	25	21	26
2	15		25	

A summary of the precision conducted internally and reported with results by both labs to the investigators is presented as percent relative percent difference (RPD) in Table 13. Also shown are the laboratories target percent RPD ranges for the various analyses. In general the precision measured as RPD is relatively low and acceptable for analysis. The higher RPD values are associated **with the dissolved total phosphorus, dissolved ortho-phosphorus, and dissolved iron determinations conducted by PPB laboratories. QA data indicate that precision is outside target boundaries from time to time for these parameters.**

Table 13 Laboratory Internal Duplicate Analysis - Relative Percent Difference

Parameter	% RPD						
	Count	Max	Min	Avg.	Std. Dev	%RPD Target	
<u>SFWMD Results</u>							
Total P	7	4.4	0.8	2.87	1.14		
Total Dis.- P	2	0.9	<	0.45	0.64		
<u>PPB Environmental Labs Results</u>							
Total P	6	14.78	1.94	9.25	4.61	0-15	
Total Dis.- P	6	16.64	<	9.21	7.17	0-15	
Dis. Ortho – P	4	35.36	<	15.91	18.60	0-20	
Dissolved Al	6	1.33	0.16	0.57	0.46	0-25	
Dissolved Fe	6	56.57	<	17.00	21.14	0-10	
Dis. Color	8	1.19	<	0.26	0.49	0-5	
Dis. Organic C	6	1.78	<	0.96	0.71	0-12	
TSS	2	0.27	<	0.14	<	0-10	
TDS	1	16.85	16.85	16.85	<	0-20	
TS	1	1.75	1.75	1.75	<	0-10	

5.7 Accuracy

Accuracy is used to compare an experimentally determined value with an accepted true value. For accuracy, samples from a duplicated source were spiked with a known mass of the constituent being measured (i.e. spiked sample). The accuracy of the experiment is then reflected in the percentage of the mass recovered in subsequent measurement. The equation used to quantify percent recovery is as follows:

$$\% \text{ Recovery} = \frac{\text{Conc}_{\text{sample+spike}} - \text{Conc}_{\text{sample}}}{\text{Conc}_{\text{spike}}} \times 100$$

A summary of the accuracy conducted internally and reported with results by both labs to the investigators is presented as percent recovery in Table 14. Also shown are the target upper and lower control limit targets for the laboratories for these analyses. The district's total and dissolved phosphorus results are limited in number but are within their standard of ± 10 percent. The contract lab had two low recovery samples (34 and 39 percent) for total phosphorus, however the remaining 6 sample spikes were between 100 and 118 percent. The contract lab total dissolved phosphorus spike recoveries were similar to the reported total phosphorus recoveries in that two samples were below 100 percent at 88 and 95 percent. However, the remaining 9 samples were above 100 percent, ranging from 109 to 120 percent. The accuracy results indicate

that the contract lab is typically measuring total and total dissolved phosphorus slightly higher than the District's laboratory, and is not achieving the District's level of accuracy.

Table 14 Laboratory Internal Spike Analysis - Percent Recovery

Parameter	% Recovery					
	Count	Max	Min	Avg.	Std. Dev	Accuracy Target
<u>SFWMD Results</u>						
Total P	7	109.8	101.8	104.89	2.68	90-110
Total Dis.- P	2	103.5	100.4	101.95	2.19	90-110
<u>PPB Environmental Labs Results</u>						
Total P	8	118	34	91.13	34.11	80-120
Total Dis.- P	11	120	88	110.55	10.26	80-120
Dis. Ortho – P	8	96	60	85.88	12.64	80-120
Dissolved Al	12	100	97	98.75	1.06	80-130
Dissolved Fe	12	103	99	101.17	1.47	90-110
Dis. Organic C	8	103	83	94.50	6.07	80-120

6.0 Conclusions

1. An anionic polymer dose of 0.5 mg/L and a coagulant dose of 1.0 to 1.5 meq/L produced acceptable floc formation and particle settling.
2. Background levels of aluminum for the NEAA water and near background for the SSTA water were achieved at coagulant doses of 1.0 to 1.5 meq/L. Lower coagulant doses would add dissolved metal above the native background concentration.
3. Background levels of iron for the NEAA water and near background for the SSTA water were achieved at coagulant dose of 1.0 to 1.5 meq/L. Lower coagulant doses would add dissolved metal above the native background concentration.
4. Cytec A-1849 anionic polymer (3percent charge, medium molecular weight) at a dose of 0.5 mg/L promoted the best overall particle and settling characteristics of three products tested. The nonionic Cytec N-1986 polymer showed adequate performance and could be a candidate for further testing should charge build-up during sludge blank formation occur in subsequent tests or future pilot studies.
5. Cytec A-1849 anionic polymer at a dose of 0.5 to 0.6 mg/L produced acceptable turbidity reduction at surface loading rates of 1.25 gpm/ft².
6. Alum doses of 1.0 meq/L for the NEAA and 1.5 meq/L of the SSTA could reduce total dissolved phosphorus below 10 ug/L. Results of ferric chloride treatment for phosphorus reduction were inconclusive.
7. Alum treatment increased dissolved aluminum concentrations by 90 to 150 ug/L Al. Ferric chloride treated waters remained near background levels.
8. The solids contact simulation determined there were no adverse affects on particle formation or settling characteristics observed with the increase in solids. The turbidity measurement between batches converged rapidly at the 1.2 gpm/ft² SLR and batch 10 with the highest solids concentration produced the same or lowest turbidity at the 0.25 gpm/ft² SLR.
9. The solids contact simulation determined the total phosphorus concentration increased in the finished water of all treated waters except for the SSTA water with alum treatment. However, alum treatment of both waters reduced the total dissolved phosphorus below the 10 ug/L. Both waters treated with ferric chloride, consistent with preceding test results increased total dissolved phosphorus in the treated water.
10. The solids contact simulation determined the alum treatment increased the background aluminum by 54 and 100 ug/L Al. Ferric chloride treatment decreased background iron by 50percent in the NEAA water but doubled the concentration in the SSTA water.
11. The solids contact simulation determined from residual measurements that a dose of 1.5 meq/L would produce an average of 51 mg/L TSS using alum and 67 mg/L TSS using

ferric chloride. After 30 minutes of thickening the percent solids of the residuals averaged 0.4 percent for alum and 0.5 percent for ferric chloride.

12. A dose of 1.5 meq/L of ferric chloride required 1 meq/L of sodium hydroxide to maintain the pH within the 7.0 to 8.range. The solids settling characteristics were greatly enhanced by adding the sodium hydroxide prior to adding the ferric chloride. Alum treatment did not require base addition at a dose of 1.5 meq/L to remain within the pH range of 6.5 to 7.0. However, if sodium hydroxide is used with alum the settling characteristics were enhanced with caustic addition immediately after alum.

7.0 Recommendations

1. Conduct laboratory analysis using a variable iron and phosphate matrix and ferric chloride from several manufacturers. The testing is to determine extent of iron interference with phosphate measurement and if ferric chloride is a potential source of phosphate.
2. A coagulant dose of 1.0 to 1.5 meq/L should be used for pilot plant initialization for solids blanket formation.
3. A polymer with a low anionic charge (3percent) and medium molecular weight at a dose of 0.5 to 0.6 mg/L active solids should be used with the coagulants to enhance settling characteristics.
4. Sodium hydroxide should be provided for pH control. The range of feed rates should be approximately 0.25 to 1.0 meq/L. Sodium hydroxide should be fed prior to ferric chloride addition and preceding alum addition when needed.
5. A surface-loading rate of 0.5 to 1.25 gpm/ft² should be the design range for the pilot units.
6. Solids storage and handling should accommodate a production rate of no less than 90 mg TSS produced per liter of water treated..